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(21) International Application Number: PCT/US94/07405 (22) International Filing Date: 30 June 1994 (30.06.94) (30) Priority Data: 93201918.5 1 July 1993 (01.07.93) EP (34) <i>Countries for which the regional or international application was filed:</i> AT et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CHRISTIE, Julie, Ann [GB/GB]; 65 Mayfair Road, West Jesmond, Newcastle upon Tyne NE2 3DN (GB). MACBEATH, Fiona, Susan [GB/GB]; Cheswick Drive, Gosforth, Newcastle upon Tyne NE3 5DF (GB). TURNER, John, Christopher [GB/GB]; 8 Collingwood Crescent, Darras Hall, Ponteland, Newcastle NE20 9DZ (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MACHINE DISHWASHING COMPOSITION CONTAINING OXYGEN BLEACH AND PARAFFIN OIL AND BENZOTRIAZOLE COMPOUND SILVER TARNISHING INHIBITORS		
(57) Abstract There is provided a bleaching composition, suitable for use in a machine dishwashing method, containing: an oxygen-releasing bleaching agent, from 0.05 % to 2.5 % by weight, preferably 0.1 % to 0.6 % by weight of a paraffin oil, from 0.005 % to 3 %, preferably from 0.02 % to 1 % and most preferably from 0.05 % to 0.5 % by weight of a benzotriazole compound. Preferably the bleaching composition forms part of a detergent composition.		

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MACHINE DISHWASHING COMPOSITION CONTAINING OXYGEN BLEACH &
PARAFFIN OIL AND BENZOTRIAZOLE COMPOUND SILVER TARNISHING INHIBITORS

Technical Field

The present invention relates to bleaching compositions, suitable for use in machine dishwashing, exhibiting good bleachable stain removal and enhanced anti silver-tarnishing properties.

Background of the Invention

Compositions designed for use in automatic dishwasher machines are well known, and a consistent effort has been made by detergent manufacturers to improve the cleaning and/or rinsing efficiency of said compositions on dishes and glassware, as reflected by numerous patent publications.

The present invention is concerned with the silver-tarnishing problem encountered when bleaching compositions which contain oxygen-bleaching species are employed in machine dishwashing methods.

The satisfactory removal of bleachable soils such as tea, fruit juice and coloured vegetable soils, such as carotenoid soils is a particular challenge to the formulator of a machine dishwashing composition. Traditionally, the

removal of such soils has been enabled by the use of bleach components such as oxygen and chlorine bleaches.

A problem encountered with the use of such bleaches is the tarnishing of any silverware components of the washload. Oxygen bleaches tend to give rise to the problem of tarnishing more than chlorine bleaches. The level of tarnishing observed can range from slight discolouration of the silverware to the formation of a dense black coating on the surface of the silverware.

The formulator thus faces the dual challenge of formulating a product which maximises bleachable soil cleaning but minimises the occurrence of tarnishing of silverware components of the washload.

The Applicants have found that the problem of tarnishing can be particularly severe when an oxygen bleaching species is employed especially when the formulation has a pH below 9.6. Oxygen bleaching species are however, preferred over chlorine bleaches for reasons of environmental compatibility.

It has been found that enhanced anti-silver tarnishing as well as good cleaning performance can be achieved through the combined use of a paraffin oil, a benzotriazole compound, and preferably control of oxygen-bleaching power.

Preferably, the rate of release of the oxygen bleach is also controlled. The rate of release of oxygen bleach is preferably rapid enough to provide satisfactory cleaning, but not so rapid that tarnishing is enabled. In particular, the rate of release of any organic peroxyacid species to the wash solution is preferably controlled.

It is an object of the present invention to provide compositions, suitable for use in machine dishwashing methods, having enhanced anti-silver tarnishing properties, as well as good cleaning performance, particularly bleachable soil removal performance.

The present compositions are based on oxygen-bleaching species, and preferably are in a compact form and have a pH of 9.6 or greater.

EPA 150 387 discloses chlorine-bleach based machine dishwashing compositions containing a paraffin wax as suds suppressor. EPA 180 088 discloses machine dishwashing compositions based on carbonates and silicates, containing paraffin oils as dust binders.

Summary of the Invention

There is provided a bleaching composition containing

- an oxygen-releasing bleaching agent
- from 0.05% to 2.5% by weight, preferably 0.1% to 0.6% by weight of a paraffin oil.
- from 0.005% to 3%, preferably from 0.02% to 1% and most preferably from 0.05% to 0.5% by weight of a benzotriazole compound.

Preferably, said oxygen-releasing bleaching agent is incorporated such that the level of available oxygen measured according to the method herein is from 0.3% to 2.5%, preferably 0.5% to 1.7% by weight.

Preferably, the rate of release of said available oxygen is such that the available oxygen is completely released from the composition in a time interval of from 3.5 minutes to 10.0 minutes, using the test protocol described in the present description.

There is also provided a detergent composition containing a detergent component preferably selected from a detergent builder compound and a surfactant, and additionally containing the bleaching composition of the invention.

Detailed Description of the Invention

The present compositions contain as essential components, an oxygen-releasing bleaching species, a benzotriazole compound and a paraffin oil. The level of available oxygen is preferably controlled. Preferably, the rate of release of available oxygen and of any organic peroxyacid bleaching species is also controlled.

Oxygen-releasing bleaching agent

The first essential feature of the compositions of the invention is a bleaching agent selected from oxygen-releasing agents such as inorganic perhydrate salts, peroxyacid bleach precursors, organic peroxyacids and mixtures thereof.

Inorganic perhydrate bleaches

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. This coating however allows for rapid release of the percarbonate bleach to the wash solution and is therefore not a suitable means for providing controlled release of the percarbonate bleach into a wash solution. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula

$\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the compositions herein. Another perhydrate is monoperoxy phthalic acid.

Inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Peroxyacid bleach precursors

Suitable peroxyacid bleach precursors typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include s, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789.

Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386. The acylation products of sorbitol, glucose and all saccharides with benzoylating agents and acetylating agents are also suitable.

Specific O-acylated precursor compounds include 2,3,3-trimethyl hexanoyl oxybenzene sulfonates, benzoyl oxybenzene sulfonates, nonanoyl-6-amino caproyl oxybenzene sulfonates, monobenzoyltetraacetyl glucose, benzoyl peroxide and cationic derivatives of any of the above, including the alkyl ammonium derivatives and pentaacetyl glucose. Phthalic anhydride is a suitable anhydride type precursor.

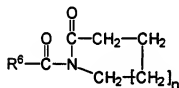
Specific cationic derivatives of the O-acyl precursor compounds include 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride, and any of the alkyl ammonium derivatives of the benzoyl oxybenzene sulfonates including the 4-(trimethyl ammonium) methyl derivative.

Useful N-acyl compounds are disclosed in GB-A-855735, 907356 and GB-A-1246338.

Preferred precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine, N-benzoyl substituted ureas and the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

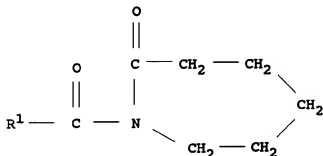
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-955735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable N-acylated lactam precursors have the formula:



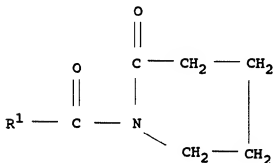
wherein n is from 0 to about 8, preferably from 0 to about 2, and R⁶ is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R¹ is phenyl.

Suitable valero lactams have the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R¹ is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at <30°C, particularly the phenyl derivatives, ie. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

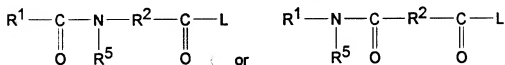
Caprolactam and valerolactam precursor materials wherein the R¹ moiety contains at least 6, preferably from 6 to about 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic clean-up. Precursor compounds wherein R¹ comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl

valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl valerolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlorobenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam, dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlorobenzoyl valerolactam, terephthaloyl divalerylactam, 4-nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

Suitable imidazoles include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing peroxyacid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

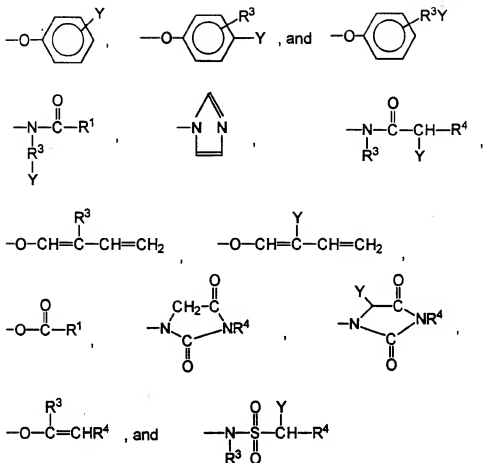
Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behavior are those in which their conjugate acid has a pKa in the range of from about 4 to about 13, preferably from about 6 to about 11 and most preferably from about 8 to about 11.

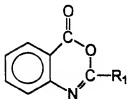
Preferred bleach precursors are those wherein R^1 , R^2 and R^5 are as defined for the amide substituted compounds and L is selected from the group consisting of:



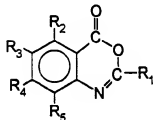
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms, R^3 is an alkyl chain containing from 1 to about 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group.

The preferred solubilizing groups are $\text{---SO}_3^-\text{M}^+$, $\text{---CO}_2^-\text{M}^+$, $\text{---SO}_4^-\text{M}^+$, $\text{---N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O---N(R}^3)_3$ and most preferably $\text{---SO}_3^-\text{M}^+$ and $\text{---CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from about 1 to about 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

Other preferred precursor compounds include those of the benzoxazin-type, having the formula:

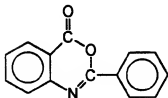


including the substituted benzoxazins of the type



wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkyl amino, COOR_6 (wherein R_6 is H or an alkyl group) and carbonyl functions.

An especially preferred precursor of the benzoxazin-type is:

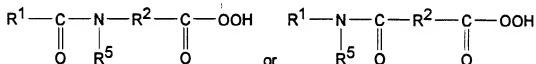


The peroxyacid bleach precursors are normally incorporated at a level of from 1% to 20% by weight, more preferably from 2% to 10% by weight, most preferably from 3% to 5% by weight of the compositions.

Organic peroxyacids

The compositions may also contain organic peroxyacids, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxy dodecanedioic acid, diperoxy tetra decanedioic acid, diperoxyhexadecanedioic acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid and its magnesium salt, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

Total Available Oxygen (AvO) Level

It has been found that, for optimal anti-silver tarnishing performance, the level of available oxygen in the present compositions, measured in units of % available oxygen by weight of the composition, should preferably be carefully controlled; the level of available oxygen should hence preferably be in the range from 0.3% to 2.5%, preferably from 0.5% to 1.7%, more preferably from 0.6% to 1.2%, most preferably from 0.7% to 1.1%, measured according to the method described hereunder.

Rate of Release of AvO

The rate of release of available oxygen is preferably also controlled; the rate of release of available oxygen from the compositions herein preferably should be such that, when using the method described hereinafter, the available oxygen is not completely released from the composition until after 3.5 minutes, preferably the available oxygen is released in a time interval of from 3.5 minutes to 10.0 minutes, more preferably from 4.0 minutes to 9.0 minutes, most preferably from 5.0 minutes to 8.5 minutes.

Method for Measuring Level of Total Available Oxygen (AvO) and Rate of Release of AvO in a Detergent Composition

Method

1. A beaker of water (typically 2L) is placed on a stirrer Hotplate, and the stirrer speed is selected to ensure that the product is evenly dispersed through the solution.
2. The bleaching composition (typically 8g of product which has been sampled down from a bulk supply using a Pascal sampler), is added and simultaneously a stop clock is started.
3. The temperature control should be adjusted so as to maintain a constant temperature of 20°C throughout the experiment.

4. Samples are taken from the bleaching solution at 2 minute time intervals for 20 mins, starting after 1 minute, and are titrated by the "titration procedure" described below to determine the level of available oxygen at each point.

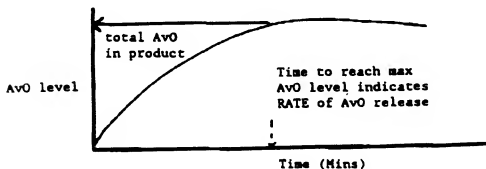
Titration Procedure

1. An aliquot from the bleaching solution (above) and 2ml sulphuric acid are added into a stirred beaker
2. Approximately 0.2g ammonium molybdate catalyst (tetra hydrate form) are added
3. 3mls of 10% sodium iodide solution are added
4. Titration with sodium thiosulphate is conducted until the end point. The end point can be seen using either of two procedures. First procedure consists simply in seeing the yellow iodine colour fading to clear. The second and preferred procedure consists of adding soluble starch when the yellow colour is becoming faint, turning the solution blue. More thiosulphate is added until the end point is reached (blue starch complex is decolourised).

The level of AvO, measured in units of % available oxygen by weight, for the sample at each time interval corresponds to the amount of titre according to the following equation

$$\frac{\text{Vol } S_2O_3 \text{ (ml)} \times \text{Molarity} \times 8}{\text{sample mass (g)}}$$

AvO level is plotted versus time as follows



Rate of release of organic peroxyacid

Where the composition contains a source of organic peroxyacid the rate of release of the organic peroxyacid species is also preferably controlled. The kinetics of release to a wash solution are preferably such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of the peroxyacid bleach is from 180 seconds to 480 seconds, more preferably from 200 seconds to 400 seconds, most preferably from 240 seconds to 360 seconds.

Rate of release of organic peroxyacid - test method

The controlled release kinetics of the organic peroxyacid herein are defined with respect to a 'T50 test method' which measures the time to achieve 50% of the ultimate concentration/level of the organic peroxyacid when a composition containing the organic peroxyacid is dissolved according to the standard conditions now set out.

The standard conditions involve a 1 litre glass beaker filled with 1000 ml of distilled water at 20°C, to which 10g of composition is added. The contents of the beaker are agitated using a magnetic stirrer set at 100 rpm. The ultimate concentration/level is taken to be the concentration/level maximum level of organic peroxyacid attained after addition of the composition to the water-filled beaker.

Suitable analytical methods are chosen to enable a reliable determination of the incidental, and ultimate in solution concentrations of the organic peroxyacid, subsequent to the addition of the composition to the water in the beaker.

Such analytical methods can include those involving a continuous monitoring of the level of concentration of the component, including for example photometric and conductrimetric methods.

Alternatively, methods involving removing titres from the solution at set time intervals, stopping the dissolution process by an appropriate means such as by rapidly reducing the temperature of the titre, and then determining the

concentration of the component in the titre by any means such as chemical titrimetric methods, can be employed.

Suitable graphical methods, including curve fitting methods, can be employed, where appropriate, to enable calculation of the the TA value from raw analytical results.

The particular analytical method selected for determining the concentration of the organic peroxyacid component, will depend on the nature of that component, and of the nature of the composition containing that component.

Controlled rate of release - means

A means may be provided for controlling the rate of release of AvO , or of organic peroxyacid to the wash solution.

Means for controlling the rate of release of organic peroxyacid may provide for controlled release of the peroxyacid bleach source itself to the wash solution. Alternatively, the means may comprise a means of inhibiting, or preventing the in situ perhydrolysis reaction which releases the peroxyacid into the solution. Such means could, for example, include controlling release of the hydrogen peroxide source to the wash solution, by for example, controlling release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable controlled release means can include coating any suitable component with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates, silicates and carbonates, including calcium carbonate and silicas.

Preferred coating material is sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 1.6 : 1 to 3.4 : 1, preferably 2.2:1 to 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10} - C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15} - C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials.

Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5×10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10} - C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10} - C_{20} mono- and diglycerol ethers and also the C_{10} - C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other means of providing the required controlled release include mechanical means for altering the physical characteristics of the bleach to control its solubility and rate of release. Suitable protocols could include compaction, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

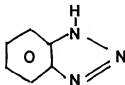
Additional protocols for providing the means of controlled release include the suitable choice of any other components of the composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

The paraffin oil

The present compositions contain from 0.05% to 2.5%, preferably from 0.1% to 0.6% by weight of the total composition of a paraffin oil typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50; preferred paraffin oil selected from predominantly branched C₂₅₋₄₅ species with a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1. A paraffin oil meeting these characteristics, having a ratio of cyclic to noncyclic hydrocarbons of about 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

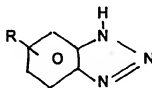
Benzotriazole compound

The compositions of the invention contain as an essential component a benzotriazole compound at a level of from 0.005% to 3%, preferably from 0.02% to 1% and most preferably from 0.05% to 0.5% of benzotriazole compound. By benzotriazole compound it is meant a compound of formula,



which is benzotriazole, and any derivatives thereof.

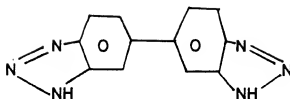
Derivatives of benzotriazole include those where the available substitution sites of the aromatic ring are wholly or partially substituted. Substituents can include, for example, straight or branched chain alkyl groups containing, for example, from one to twenty carbon atoms in the alkyl chain. Other substituents can include -OH, -SH, phenyl or halogen groups. Other derivatives include bis-benzotriazoles. British Patent, GB-A-1,065,995 describes suitable substituted benzotriazoles of formula



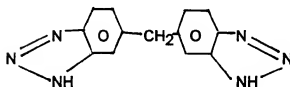
where R is a straight or branched chain alkyl group containing from two to twenty atoms, and a process for making such compounds. British Patent, GB-A-1,226,100 describes compositions containing 4, 5, 6, 7-tetrahydro-benzotriazole compounds, which are also suitable for inclusion in the compositions of the invention.

British Patent GB-A-1, 180, 437 describes suitable bis-benzotriazoles having the formula

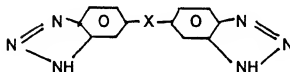
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and



and



wherein X represents a straight-chain alkylene group containing from one to six carbon atoms in the chain, being substituted with one or two alkyl groups containing from one to four carbon atoms where the alkylene group contains only one carbon atom, or being substituted with one or more alkyl groups containing from one to four carbon atoms where the alkylene group contains two or more carbon atoms, or being unsubstituted where the alkylene group contains two or more carbon atoms; a 1:1-cycloalkyl residue containing at least five carbon atoms; a carbonyl group; a sulphurlyl group, an oxygen atom; or a sulphur atom.

Detergent Compositions

The bleaching compositions of the invention may form part of a detergent composition containing detergent components such as detergent builder compounds, surfactants, heavy metal ion sequestrants, enzymes, lime soap dispersants, suds controlling agents and mixtures thereof.

Builder

A highly preferred component of the detergent compositions in accord with the present invention is a detergent builder compound preferably present at a level of from 1% to 80% by weight, more preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

The level of alkali metal carbonate or bicarbonate in the present compositions should preferably be inferior to 7%, more preferably inferior to 5%, by weight of the total composition. Most preferably the present composition should be free of alkali metal carbonate or bicarbonate species.

Suitable detergent builder compounds include, but are not restricted to monomeric polycarboxylates, or their acid forms homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, silicates and mixtures of any of the foregoing.

Suitable monomeric or oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

The logarithmic acidity constant is defined by reference to the equilibrium



where A is the fully ionized carboxylate anion of the builder salt.

The equilibrium constant for dilute solutions is therefore given by the expression

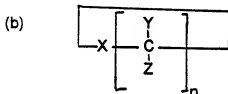
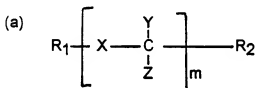
$$K_1 = \frac{[HA]}{[H^+][A^-]}$$

and $pK_1 = \log_{10} K$.

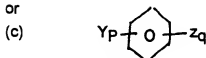
For the purposes of this specification, acidity constants are defined at 25°C and at zero ionic strength. Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London); where doubt arises they are determined by potentiometric titration using a glass electrode.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates having the general formulae



or



wherein R_1 represents H, C₁₋₃₀ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethylenoxy moiety containing up to 20 ethyleneoxy groups; R_2 represents H, C₁₋₄ alkyl, alkenyl or hydroxy alkyl, or alkaryl, sulfo, or phosphono groups; X represents a single bond; O; S; SO₂; or NR₁; Y represents H; carboxy; hydroxy; carboxymethoxy; or C₁₋₃₀ alkyl or alkenyl optionally substituted by hydroxy or carboxy groups; Z represents H; or carboxy; m is an integer from 1 to 10; n is an integer from 3 to 6; p, q are integers from 0 to 6, p + q being from 1 to 6; and wherein, X, Y, and Z each have the same or different representations when repeated in a given

molecular formula, and wherein at least one Y or Z in a molecule contain a carboxyl group.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis-cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of detergent compositions in accordance with the present invention.

Other suitable water soluble organic salts are the homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000. These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Water-soluble detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), and sulfates. The levels of incorporation of carbonates or bicarbonates or mixtures thereof, is however preferably limited to less than 7% by weight of the composition.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C.

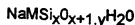
Specific examples of phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Suitable silicates include the water soluble sodium silicates with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 2.0 is the most preferred silicate.

Silicates are preferably present in the machine dishwashing detergent compositions at the invention at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight, most preferably from 12% to 25% by weight.

Examples of such less water soluble builders include the crystalline layered silicates and the largely water insoluble sodium aluminosilicates.

Crystalline layered sodium silicates have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α -, β -, γ - and δ -forms of $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is δ - $\text{Na}_2\text{Si}_2\text{O}_5$, NaSKS-6.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof. The primary requirement is that the material should contain at least one functional acidic group of which the pK_a should be less than 9, providing a capability for at least partial neutralisation of the hydroxyl ions released by the crystalline layered silicate.

The incorporation in the particulate of other ingredients additional to the crystalline layered silicate and ionisable water soluble compound can be advantageous particularly in the processing of the particulate and also in enhancing the stability of detergent compositions in which the particulates are included. In particular, certain types of agglomerates may require the addition of one or more binder agents in order to assist in binding the silicate and ionisable water soluble material so as to produce particulates with acceptable physical characteristics.

The crystalline layered sodium silicate containing particulates can take a variety of physical forms such as extrudates, marumes, agglomerates, flakes or compacted granules. A preferred process for preparing compacted granules comprising crystalline layered silicate and a solid, water-soluble ionisable material has been disclosed in the commonly assigned British Application No. 9108639.7 filed on 23 April 1991.

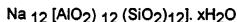
Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_x[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot \text{XH}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 200 mg equivalent of CaCO_3 water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of CaCO_3 / litre / minute / (g/litre) [2 grains Ca^{++} / gallon/ minute/ gram/ gallon] of aluminosilicate (anhydrous basis), and which generally lies

within the range of from 130 mg equivalent of CaCO_3 / litre/ minute/ (gram/litre) [2 grains/ gallon/ minute/ (gram/ gallon)] to 390 mg equivalent of CaCO_3 / litre/ minute/ (gram/litre) [4 grains/ gallon/ minute/ (gram/ gallon)], based on calcium ion hardness.

Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of CaCO_3 /litre/ minute/ (gram/litre) [4 grains/gallon/minute/ (gram/ gallon)].

The aluminosilicate ion exchange materials can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ has the formula $\text{Na}_6 [(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

The heavy metal ion sequestrant

In a preferred aspect, the detergent compositions further contain narrowly defined levels of a heavy metal ion sequestrant, such levels being in the range 0.005% to 3%, preferably 0.01 to 1%, most preferably 0.05% to 0.8%, by weight of the total composition.

Suitable heavy-metal sequestrant for use herein include organic phosphonates, such as amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy disphosphonates, nitrilo trimethylene phosphonates.

Preferred among above species are diethylene triamine penta (methylene phosphonate), hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

The phosphonate compounds may be present either in their acid form or as a complex of either an alkali or alkaline metal ion, the molar ratio of said metal ion to said phosphonate compound being at least 1:1. Such complexes are described in US-A-4,259,200. Preferably, the organic phosphonate compounds are in the form of their magnesium salt.

Other suitable sequestrant for inclusion in the compositions in accordance with the invention include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid or the water soluble alkali metal salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_3EDDS . Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg_2EDDS . The magnesium complexes are the most preferred for inclusion in compositions in accordance with the invention.

Still other suitable sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EPA 317 542 and EPA 399 133.

The heavy metal ion sequestrant herein can consist of a mixture of the above described species.

Optional chlorine bleach components

Chlorine bleaches include the alkali metal hypochlorites and chlorinated cyanuric acid salts. The use of chlorine bleaches in the composition of the invention is optional and preferably minimized, and more preferably the present compositions contain no chlorine bleach.

Surfactant

A highly preferred component of the compositions of the invention is a surfactant system comprising surfactant selected from anionic, cationic,

nonionic ampholytic and zwitterionic surfactants and mixtures thereof. The surfactant system is preferably present at a level of from 0.5% to 30% by weight, more preferably 1% to 25% by weight, most preferably from 2% to 20% by weight of the compositions.

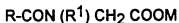
A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981. A listing of surfactants typically included in automatic dishwashing detergent compositions is given in EP-A-0414 549.

Sulphonate and sulphate surfactants are useful herein. Sulphonates include alkyl benzene sulphonates having from 5 to 15 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₆-C₁₈ fatty source. Preferred sulphate surfactants are alkyl sulphates having from 6 to 16, preferably 6 to 10 carbon atoms in the alkyl radical.

Useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. The cation in each instance is again an alkali metal, preferably sodium. The alkyl sulfate salts may be derived from natural or synthetic hydrocarbon sources.

The C₆-C₁₆ alkyl ethoxysulfate salt comprises a primary alkyl ethoxysulfate which is derived from the condensation product of a C₆-C₁₆ alcohol condensed with an average of from one to seven ethylene oxide groups, per mole. Preferred are the C₆-C₁₀ alkyl ethoxysulfate salts with an average of from one to five ethoxy groups per mole.

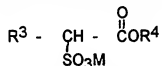
Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula



wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C₁₂-C₁₄), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Another class of anionic surfactants useful herein are the alkyl ester sulfonate surfactants which include linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactants have the structural formula:



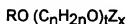
wherein R³ is a C₈-C₂₀ hydrocarbonyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbonyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

One preferred class of nonionic surfactants useful in the present invention comprises the water soluble ethoxylated C₆-C₁₆ fatty alcohols and C₆-C₁₆ mixed ethoxylated/propoxylated fatty alcohols and mixtures thereof. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₆ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₆ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Thus C₆-C₁₆ alcohol itself can be obtained from natural or synthetic sources. Thus, C₆-C₁₆ alcohols, derived from natural fats, or Ziegler olefin build-up, or OXO synthesis can form suitable sources for the alkyl group. Examples of synthetically derived materials include Dobanol 25 (RTM) sold by Shell Chemicals (UK) Ltd which is a blend of C₁₂-C₁₅ alcohols, Ethyl 24 sold by the Ethyl Corporation which is a blend of C₁₂-C₁₅ alcohols, and a blend of C₁₃-

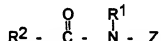
C₁₅ alcohols in the ratio 67% C₁₃, 33% C₁₅ sold under the trade name Lutensol by BASF GmbH and Synperonic (RTM) by ICI Ltd., and Lial 125 sold by Liquichimica Italiana. Examples of naturally occurring materials from which the alcohols can be derived are coconut oil and palm kernel oil and the corresponding fatty acids:

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 6 to 16 carbon atoms preferably from 6 to 14 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

Another preferred nonionic surfactant is a polyhydroxy fatty acid amide surfactant compound having the structural formula:



wherein R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (ie., methyl); and R² is a C₅-C₁₅ hydrocarbyl, preferably straight chain C₅-C₁₃ alkyl or alkenyl, more preferably straight chain C₅-C₁₁ alkyl or alkenyl, most preferably straight chain C₅-C₉ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycidyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose

corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, or tallowamide.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl or 1-deoxymannityl, or 1-deoxymalto-triitityl. Preferred compounds are N-methyl N-1deoxyglucityl $\text{C}_{14}-\text{C}_{18}$ fatty acid amides.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_6-C_{20} , preferably C_6-C_{10} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_6-C_{16} , preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Enzymes

Another optional ingredient useful in detergent compositions is one or more enzymes.

Preferred enzymatic materials include amylases, neutral and alkaline proteases, lipases, and esterases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase and Savinase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands). Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.005% to 2% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of B licheniformis, described in more detail in GB 1,269,839 (Novo). Preferred commercially available amylases include for example, Rapidase, sold by International Bio-Synthetics Inc, and Termamyl, sold by Novo Industries A/S. The invention at a level of from 0.001% to 2% active enzyme by weight of the composition.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Lime soap dispersant

Another optional ingredient is a lime soap dispersant compound, present at a level of from 0.05% to 40% by weight, more preferably 0.1% to 20% by weight, most preferably from 0.25% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions.

Preferred lime soap dispersants include C13-15 ethoxylated alcohol sulphates with an average degree of ethoxylation of 3.

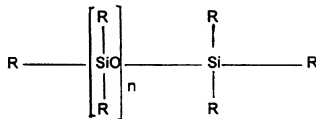
Another optional component of the detergent compositions of the invention is a silicone suds controlling agent present at levels of from 0.01% to 5% by weight, more preferably from 0.05% to 3% by weight, most preferably from 0.05% to 1% by weight of the composition.

Suds controlling agent

By silicone suds controlling agent it is meant any suds controlling agent which comprises a silicone antifoam compound. Thus silicone suds controlling agents include agents containing silicone-silica mixtures and particulates in which the silicone, or silicone-silica mixture, is incorporated in a water-soluble or water-dispersible carrier material. Alternatively, the silicone suds controlling agents may comprise silicone, or silicone-silica mixtures dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components of the detergent composition.

In industrial practice the term "silicone" has become a generic term which encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types.

Generally, the silicone antifoam compounds can be described as siloxanes having the general structure :



where each R independently can be an alkyl or an aryl radical. Examples of such substituents are methyl, ethyl, propyl, isobutyl, and phenyl. Preferred polydiorganosiloxanes are polydimethylsiloxanes having trimethylsilyl endblocking units and having a viscosity at 25°C of from 5×10^{-5} m²/s to 0.1 m²/s i.e. a value of η in the range 40 to 1500. These are preferred because of their ready availability and their relatively low cost.

A preferred type of silicone suds controlling agent useful in the compositions herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica made by the gelformation technique. The silica particles suitable have an average particle size of from 0.1 to 50 micrometers, preferably from 1 to 20 micrometers and a surface area of at least 50m²/g. These silica particles can be rendered hydrophobic by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. It is preferred to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. The suds controlling agents for inclusion in the detergent compositions in accordance with the invention suitably contain an amount of silica such that the weight ratio of silica to silicone lies in the range from 1:100 to 3:10, preferably from 1:50 to 1:7.

A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated)silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

Another preferred silicone suds controlling agent is disclosed in Bartollota et Al. US Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC0544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

A highly preferred silicone suds controlling agent is a particulate of the type disclosed in EP-A-0210731 comprising a silicone antifoam and an organic material having a melting point in the range 50° to 85°C, wherein the organic material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses similar particulate suds controlling agents wherein the organic material however, is a

fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred silicone suds controlling agents are described in copending European Application 91870007.1 in the name of the Procter and Gamble Company which discloses granular suds controlling agents comprising a silicone antifoam compound, a carrier material an organic coating material and glycerol at a weight ratio of glycerol: silicone antifoam compound of 1:2 to 3:1. Copending European Application 91201342.0 also discloses highly preferred granular suds controlling agents comprising a silicone antifoam compound, a carrier material, an organic coating material and crystalline or amorphous aluminosilicate at a weight ratio of aluminosilicate: silicone antifoam compound of 1:3 to 3:1. The preferred carrier material in both of the above described highly preferred granular suds controlling agents is starch.

The preferred methods of incorporation of the silicone suds controlling agents comprise either application of the silicone suds controlling agent in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the silicone suds controlling agents into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds controlling agents as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds controlling particulates are disclosed in the previously mentioned Bartolotta et al US Patent No. 3,933,672.

Other optional ingredients suitable for inclusion in the compositions of the invention include antiredeposition, and soil-suspension agents, corrosion inhibitors, perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes, liquids, gels and tablets, granular forms being preferred.

The bulk density of granular compositions in accordance with the present invention is typically of at least 650 g/litre, more usually at least 700 g/litre and more preferably from 800 g/litre to 1200 g/litre.

Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide the bulk density in g/litre. Replicate measurements are made as required.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

Generally, if the detergent compositions are in liquid form the liquid should be thixotropic (ie; exhibit high viscosity when subjected to low stress and lower viscosity when subjected to high stress), or at least have very high viscosity, for example, of from 1,000 to 10,000,000 centipoise. In many cases it is desirable to include a viscosity control agent or a thixotropic agent to provide a suitable

liquid product form. Suitable thixotropic or viscosity control agents include methyl cellulose, carboxymethylcellulose, starch, polyvinyl, pyrrolidone, gelatin, colloidal silica, and natural or synthetic clay minerals.

Pasty compositions in accordance with the invention generally have viscosities of about 5,000 centipoise and up to several hundred million centipoise. In order to provide satisfaction pasty compositions a small amount of a solvent or solubilizing agent or of a gel-forming agent can be included. Most commonly, water is used in this context and forms the continuous phase of a concentrated dispersion. Certain nonionic surfactants at high levels form a gel in the presence of small amount of water and other solvents. Such gelled compositions also envisaged in the present invention.

pH of the compositions

The pH of a 1% solution of the present compositions is preferably from 9.6 to 12, preferably from 9.8 to 11.5, most preferably from 10.0 to 11.0.

Making process for the compositions herein

A preferred making process for the compositions herein comprises pre-mixing of the paraffin oil with a dispersing agent and the resultive intimate pre-mix being sprayed onto the remainder of the composition. The dispersing agent can advantageously consist of a nonionic surfactant such as described hereinabove, which therefore serves two functions in the present composition.

A preferred dispersing agent is Plurafac LF404 sold by BASF.

An alternate route consists in spraying the intimate mixture of paraffin oil and dispersing agent onto the particles of bleaching agent, resulting in a reduction in the rate of dissolution in water of said bleaching agent and therefore providing a control over the rate of release of available oxygen. The coated particles of bleaching agent are then dry-mixed with the remainder of the composition.

In another process embodiment herein, the particle of bleaching agents are compacted before being dry-mixed with the remainder of the composition .

This technique slows down the dissolution rate in water, and is therefore advantageously applied to otherwise fast dissolving species like perborate monohydrate.

In this embodiment, the paraffin oil is typically compacted along with the bleaching species, and optionally other ingredients like sodium sulphate and/or binders. The resulting particles are then dry-mixed with the remainder of the ingredients.

EXAMPLES

The following examples illustrate the present invention.

In the following detergent compositions, the abbreviated identifications have the following meanings:

Citrate:	Tri-Sodium citrate dihydrate
Phosphate:	Sodium tripolyphosphate
MA/AA:	Copolymers of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Silicate:	Amorphous Sodium Silicate ($\text{SiO}_2\text{:Na}_2\text{O}$ ratio normally follows)
Protease:	Proteolytic enzyme sold under the trade name Savinase by Novo Industries A/S
Amylase:	Amylolytic enzyme sold under the trade name Termamyl by Novo Industries A/S
Nonionic:	C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the trade name Plurafac LF404 by BASF GmbH.
Anionic :	C ₆₋₁₀ alkyl ethoxysulfate with 1-5 ethoxy groups per mole
Sulphate:	Anhydrous Sodium Sulphate
TAED:	Tetraacetyl ethylene diamine
DTPMP :	Diethylene triamine penta (methylene phosphonic acid)
EDDS :	Ethylene Diamine-N,N Disuccinic acid
Benzotriazole :	Benzotriazole

The following machine dishwashing detergents according to the invention are prepared (parts by weight):

Ingredients	Parts by weight			
	I	II	III	IV
citrate	38.0	35.0	40.0	35.0
MA/AA	4.0	6.0	2.0	4.0
2 ratio silicate (2.0 ratio)	26.0	30.0	20.0	30.0
AvO level	0.8	0.8	1.0	1.0
Perborate monohydrate (1)	-	5.05	-	-
Perborate tetrahydrate	8.0	-	9.0	9.0
TAED	2.5	2.2	3.0	2.2
Paraffin oil (2)	0.5	0.5	0.3	0.3
Protease	2.0	2.5	2.2	2.0
Amylase	1.5	0.5	1.0	1.0
Lipase	-	-	2.0	-
Nonionic (3)	1.54	1.0	1.5	1.5
Anionic	-	3.0	-	-
DTPMP	0.1	0.2	-	-
Benzotriazole	0.1	0.1	0.1	0.2
EDDS	0.1	-	0.15	-
Limesoap dispersant (4)	-	-	2.5	-
Suds suppressor	-	1.0	-	-
Sulphate	balance to 100			
pH	10.7	10.7	10.7	10.7

(1) Pre-compacted before incorporation

(2) WINOG 70 ex Wintershall

(3) Pre-mixed with the paraffin oil before incorporation

(4) Lutensol AO12 ex BASF

Comparative testing 1

The following comparative testing was conducted; Composition A, in accord with the invention was compared for anti-silver tarnishing performance, to Compositions B and C. Composition B contains no paraffin oil or benzotriazole. Composition B contains paraffin but no benzotriazole.

Ingredients	Parts by weight		
	Composition A	Composition B	Composition C
citrate	38.0	38.0	38.0
MA/AA	4.0	4.0	4.0
2 ratio silicate (2.0 ratio)	26.0	26.0	26.0
AvO level	0.8	1.5	0.8
Perborate monohydrate	-	11.0	-
Perborate tetrahydrate	8.0	-	8.0
TAED	3.8	2.5	3.8
Paraffin oil	0.5	-	0.5
Benzotriazole	0.15	-	-
Protease	2.0	2.0	2.0
Amylase	1.5	1.5	1.5
Nonionic	1.5	1.5	1.5
Sulphate	—balance	to 100 —	—

The test protocol employed comprised machine testing, using a Bosch Siemens dishwasher, 20g product dosage, 65°C economy cycles, and 20 cycles.

Performance was graded by 4 expert panellists through visual inspection according to the following scale :

where

- 0 = no tarnish (shiny silver)
- 1 = very slight tarnish
- 2 = tarnish
- 3 = very tarnished
- 4 = severe tarnish (black coverage)

Results were as follows : (average of the 4 gradings from the panellists)

Comp. A	Comp. B	Comp. C
0.0	4.0	1.5

Composition A shows superior anti-silver tarnishing performance over Compositions B and C, in accord with the invention.

CLAIMS

1. A bleaching composition containing
 - an oxygen-releasing bleaching agent
 - from 0.05% to 2.5% by weight of a paraffin oil
 - from 0.005% to 3% by weight of a benzotriazole compound.
2. A composition according to claim 1 wherein the level of oxygen-releasing bleaching agent is such that the level of available oxygen measured according to the method herein is from 0.3% to 2.5%.
3. A composition according to either of claims 1 or 2 wherein the rate of release of the available oxygen is such that the available oxygen is completely released from the composition in a time interval of from 3.5 minutes to 10 minutes, using the test protocol described in the present description.
4. A composition according to claims 1-3 containing a source of organic peroxyacid wherein according to the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of the peroxyacid is from 180 seconds to 480 seconds.
5. A composition according to claims 1-4 wherein the paraffin oil is present at a level of from 0.1% to 0.6%.
6. A composition according to claims 1-5 wherein the paraffin oil is selected from predominantly branched aliphatic hydrocarbons having from 20 to 50, preferably 25 to 45 carbon atoms, with a ratio of cyclic to noncyclic hydrocarbons of from 1:5 to 1:1.
7. A composition according to claims 1-6 wherein the benzotriazole compound is present at levels of from 0.02% to 1%.

8. A composition according to claims 1-7 wherein the benzotriazole compound is present at levels of from 0.05% to 0.5%.
9. A composition according to claims 1-8 wherein the benzotriazole compound is benzotriazole.
10. A composition according to claims 1-9 wherein the oxygen-releasing bleaching agent comprises in combination an inorganic perhydrate salt and a peroxyacid bleach precursor.
11. A composition according to claims 1-10 containing a heavy metal ion sequestrant at a level of from 0.005% to 3% by weight.
12. A detergent composition containing a detergent component selected from a detergent builder compound and a surfactant, additionally containing a composition according to any of claims 1-11.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07405

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C11D 7/18, 7/24, 7/32; C23G 1/18

US CL : 252/102, 139, 390, 524

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/102, 139, 390, 524


Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,089,162 [RAPISARDA ET AL.] 18 February 1992 See Col. 4, lines 15-25; Col. 9, lines 31-39 and the Abstract.	1-4
Y	US, A, 4,919,834 [CHEN ET AL.] 24 April 1990 See Col. 8, lines 20-23; Col. 11, lines 12-21 and Col. 1, lines 15-13.	1-4
Y	US, A, 4,620,936 [KIELMANET ET AL.] 04 November 1986 See the Abstract and Col. 4, lines 16-24.	1-4
Y	DE, A, 4121307-A1 [KRUSE ET AL.] 07 January 1993 See the Abstract and Page 4, lines 11-21.	1-4

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* "A" document defining the general state of the art which is not considered to be of particular relevance	* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* "E" earlier document published on or after the international filing date	* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
* "O" document referring to an oral disclosure, use, exhibition or other means	
* "P" document published prior to the international filing date but later than the priority date claimed	* "G" document member of the same patent family

Date of the actual completion of the international search 22 AUGUST 1994	Date of mailing of the international search report SEP 08 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  DENNIS L. ALBRECHT
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/07405

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.